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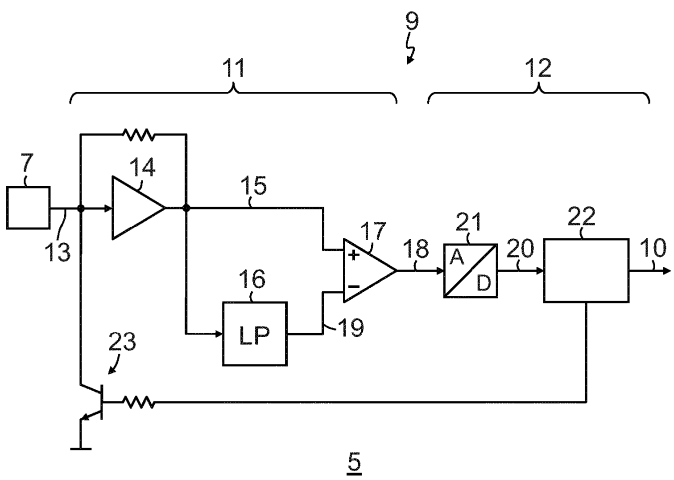
(54) Thermal conductivity detector circuit and method for operating the same

(57) A thermal conductivity detector (5) comprises:
a measuring cell (7) through which a sample fluid in a reference carrier fluid stream flows and which contains a detector element for generating a detector signal (13),
an analog signal processing portion (11) including an amplifier (14) for amplifying the detector signal (13), a low-pass filter (16) for providing a running average (19) of the amplified detector signal (15), and a subtracting means (17) for generating a difference signal (18) from the amplified detector signal (15) and the running average (19), and
a digital signal processing portion (12) for digitizing and digitally processing the difference signal (18).

To improve the thermal conductivity detector for use in gas chromatography without the need of an additional reference cell it further comprises a switch (23) controllable to short-circuit the input of the amplifier (14),
the digital signal processing portion (12) being adapted to calculate a transfer function of the analog signal processing portion (11) from the digitized difference signal (20) received in response to short-circuiting the input of the amplifier (14) at a given time when solely the reference carrier fluid passes the measuring cell (7), and
the digital signal processing portion (12) being further adapted to recover the detector signal by deconvoluting the digitized difference signal (20) with the transfer function.

FIG. 2



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Description

[0001] The present invention relates to a thermal conductivity detector and a method for operating the same.

[0002] Thermal conductivity detectors are used to detect certain liquid or gaseous substances (fluids) on the basis of their characteristic thermal conductivity, particularly in gas chromatography. There, components or substances of a gas mixture are separated by passing a sample of the gas mixture in a carrier gas (mobile phase) through a separation column containing a stationary phase. The different components interact with the stationary phase which causes each component to elute at a different time, known as the retention time of the component. The separated substances are detected by a thermal conductivity detector which has a measuring cell with an appropriate detector element, e.g. an electrically heated filament disposed in a measurement channel. Depending on the thermal conductivity of the substance flowing past the heated filament, more or less heat is diverted from the heating filament to the wall of the measurement channel, and the heating filament is correspondingly cooled to a greater or lesser degree. As a result of the cooling of the heating filament, its electrical resistance changes, which is detected.

[0003] For this purpose, the heating filament may be disposed in a measuring bridge, which contains additional resistors and an additional heating filament in a reference channel through which a reference fluid flows (e.g. US 5,756,878, Fig. 8). The thermal conductivity of the substance passing the heating filament is obtained from an amount of energy which is supplied to the measuring bridge and is controlled to maintain the temperature of the heating filament at a predetermined temperature. Instead of the resistors, further filaments may be provided which are fluidically parallel or in series with the filaments in the measurement channel and the reference channel, respectively.

[0004] From e.g. Fig. 2 of US 2008/0291966 A1 a thermal conductivity detector is known that includes the measuring cell as well as a reference cell. The measuring cell is passed through by the carrier gas stream whereas the reference cell is passed solely by the carrier gas. The detector signals provided by the respective thermal conductivity detector elements of the measuring and reference cells are amplified and then subtracted from each other to obtain a difference signal that is only representative of the sample. For further digital processing, the difference signal must be digitized with a high resolution of, e.g., 24 bit which corresponds to a dynamic range of 144 dB. Thus, noise and drift characteristics of the difference signal are very important.

[0005] A problem with the additional reference cell is that it may have noise, drift and physical response characteristics that do not exactly match or track those of the measuring cell. These characteristics work against the quality of the detector signal from the measuring cell because they may introduce degradation in the difference signal when the reference signal is subtracted from the detector signal.

[0006] Additionally, chromatography applications can sometimes be limited by the number of reference cells available for measurement. Groups of detector cells are often assigned to one fixed reference cell. Thus, the ability to use any detector without a reference constraint would allow for far greater freedom to the application chemist and would also reduce complexity and costs.

[0007] It is therefore an object of the present invention to provide a thermal conductivity detector for use in gas chromatography without the need of an additional reference cell.

[0008] It is further an object of the present invention to provide a method for operating a thermal conductivity detector without the need of an additional reference cell.

[0009] According to the invention, this object is achieved by the thermal conductivity detector defined in claim 1 or the method of claim 2.

[0010] Thus, subject of the invention is a thermal conductivity detector comprising:

> a measuring cell to be passed through by a sample fluid in a reference carrier fluid stream, the measuring cell containing at least one thermal conductivity detector element and providing a detector signal,
> an analog signal processing portion including an amplifier for amplifying the detector signal, a low-pass filter for providing a running average of the amplified detector signal, and a subtracting means for generating a difference signal from the amplified detector signal and the running average,
> a digital signal processing portion for digitizing and digitally processing the difference signal, and
> a switch controllable to short-circuit the input of the amplifier,
> the digital signal processing portion being adapted to calculate a transfer function of the analog signal processing means from the digitized difference signal received in response to short-circuiting the input of the amplifier at a given time when solely the reference carrier fluid passes the measuring cell, and
> the digital signal processing portion being further adapted to recover the detector signal in a digital form by deconvoluting the digitized difference signal with the transfer function.

[0011] The terms "amplifier" and "subtracting means" referred to are to be understood in a generic sense and also include, e.g., an amplifier of inverting type followed by adding means.

[0012] The subject of invention is also a method for operating a thermal conductivity detector comprising:

> passing a sample fluid in a reference carrier fluid stream through a measuring cell and generating a detector signal by means of a thermal conductivity detector element,

processing the detector signal by an analog signal processing portion including amplifying the detector signal, providing a running average of the amplified detector signal by low-pass filtering, and generating a difference signal from the amplified detector signal and the running average, and
digitizing and digitally processing the difference signal, the method further comprising, as an initial step, short-circuiting the input of the amplifier, and calculating a transfer function of the analog signal processing portion from the digitized difference signal received in response to short-circuiting the input of the amplifier at a given time when solely the reference carrier fluid passes the measuring cell,
the step of digitally processing the difference signal including recovering the detector signal in a digital form by deconvoluting the digitized difference signal with the transfer function.

[0013] The term "running average" should not be understood in the usually narrow sense of "moving average" but in the broader sense of a DC component or baseline of the amplified detector signal. According to the invention, the running average or DC component or baseline is removed from the amplified detector signal to obtain a difference signal that is only representative of the sample and therefore can be effectively digitized with a high resolution. The analog low-pass filter, however, does not only remove the DC component or baseline but also affects higher frequency signal portions representing the sample. In order to reduce or correct this effect, the detector signal is recovered or restored in a digital form by deconvoluting (unfolding) the digitized difference signal with the transfer function of the analog signal processing portion of the thermal conductivity detector. The transfer function is determined in advance by applying a step function or impulse function to the analog signal processing portion at a given time when solely the reference carrier fluid passes the measuring cell and evaluating the step or impulse response. The step or impulse function is performed by a switch for short-circuiting the input of the analog signal processing portion, i.e. the input of the amplifier, so that the signal path of the detector signal is unchanged. When the switch is open, it has no effect (including noise effects) on the thermal conductivity detector element. When the switch is closed, it shorts the detector element and the amplifier responds with a change in output.

[0014] When used in a process gas chromatograph, the switch is closed at the start of each or every n-th chromatographic cycle for a short time while solely the reference carrier gas flows through the measuring cell. The timing of the switch may be controlled by the digital signal processing portion of the thermal conductivity detector, which digital signal processing portion in turn may be controlled by a higher-level control system of a gas chromatograph.

[0015] As the thermal conductivity detector according to the invention shows its advantages in particular in gas chromatography, a gas chromatograph comprising at least one thermal conductivity detector as described so far is a further subject of the invention.

[0016] The invention will now be described by way of example and with reference to the accompanying drawing, in which

Fig. 1 is a simplified schematic block diagram of an exemplary gas chromatograph having a thermal conductivity detector in accordance with the invention, and

Fig. 2 is an exemplary embodiment of the thermal conductivity detector according to the invention.

[0017] Fig. 1 shows a gas chromatograph in which a carrier gas 1 is delivered to an injector 2, loaded there with a sample of a gas mixture 3 to be analyzed and subsequently introduced into a separation device 4 such as a single separation column or a complete system of separation columns. The separated components or substances of the gas mixture emerging successively from the separation device 4 travel to a thermal conductivity detector 5. There, the separated gas components are conveyed in a measurement channel 6 of a measuring cell 7 past a detector element 8 such as an electrically heated heating filament. Depending on the thermal conductivity of the gas components respectively flowing past in comparison with that of the carrier gas, more or less heat is transferred from the heating filament 8 to the channel wall so that the heating filament 8 is correspondingly cooled or heated. As a result, the electrical resistance of the heating filament 8 changes, which change is detected in an evaluation device 9 of the detector 5. To this end, the heating filament 8 may be arranged in a measurement bridge in a manner known per se (not shown). The evaluation device 9 provides an output 10 that indicates the presence and amount of the gas components passing the heating filament 7.

[0018] Fig. 2 shows in a simplified schematic diagram an exemplary embodiment of the thermal conductivity detector 5 including the measuring cell 7 and the evaluation device 9, which consists of an analog signal processing portion 11 and a digital signal processing portion 12. The detector element 8 (Fig. 1) provides a detector signal 13 that is conditioned and amplified by an input-side amplifier 14 of the analog signal processing portion 11. The amplified detector signal 15 is fed once directly and once via a low-pass filter 16 to a subtracting means 17, which is here in the form of a differential amplifier. The subtracting means 17 generates a difference signal 18 from the amplified detector signal 15 and its running average 19 formed by the low-pass filter 16. The analog difference signal 18 is then converted to a digital signal 20 by an analog-to-digital converter 21 and passed to a digital signal processor 22 for further processing and generating the output 10.

[0019] A switch 23, here in the form of an NPN transistor, is arranged between the input of the amplifier 14 and ground. The switch 23 is controlled by the digital signal processor 22 to close and thus short-circuit the input of the amplifier 14 at the start of each or every n-th chromatographic cycle for a short time while solely the reference carrier gas 1 flows through the measuring cell 7. The amplifier 14 responds with a rapid change in its output, effectively being a step function. The analog signal processing portion 11 responds by what is the convolution of the step function and the impulse response of the analog signal processing portion 11 itself. Thus, the transfer function f(n) of the low-pass filter 16 and the transfer function 1-f(n) of the combined low-pass filter 16 and subtracting means 17 can be calculated from the digitized difference signal 20 received by the digital signal processor 22 in response to the step function. This allows for characterizing and, if necessary, adapting the low-pass filter 16.

[0020] When a chromatographic cycle starts and the sample in the carrier gas stream passes through the measuring cell 7, the switch 23 is open and has no effect on the detector element 8 and the subsequent processing electronics. As the low-pass filter 16 not only removes a DC component from the amplified detector signal 15 but also affects higher frequency signal portions which represent the sample, the difference signal 18 will be distorted correspondingly. The digital signal processor 22 therefore restores the detector signal in a digital form by deconvoluting the digitized difference signal 20 with the transfer function 1-f(n) of the analog signal processing portion 11.

[0021] The operating sequence of the thermal conductivity detector 5 may be as follows:

1. Wait until previous sample is cleared from the separation device 4 and the tubing to the measuring cell 7, such that only carrier gas 1 is flowing.
2. Apply step function (close switch 23).
3. Acquire transfer function of the analog signal processing portion 11 from the step response.
4. Remove step function (open switch 23).
5. Allow system to settle after removal of step function.
6. Start chromatographic cycle.
7. End of chromatographic cycle.
8. Restore detector signal by deconvoluting the received difference signal 20 with the transfer function of the analog signal processing portion 11.
9. Decide if low-pass filter 16 needs to be characterized again; if so go back to step 1.
10. Else: Go back to step 6.

[0022] One significant advantage of the invention is that the operating sequence of the thermal conductivity detector and thus of the gas chromatograph is closer to being a continuous process because the low-pass filter time constant needs to be set only at some multiple of the widest chromatographic peak of interest. This keeps from having a low pass filter that requires many seconds or even minutes to settle and be ready for a measurement. DC drift of the low-pass filter 16 is also less important since this would be calibrated out in the transfer function.

Claims

1. A thermal conductivity detector (5) comprising:

a measuring cell (7) to be passed through by a sample fluid in a reference carrier fluid stream (1), the measuring cell (7) containing at least one thermal conductivity detector element (8) and providing a detector signal (13),
an analog signal processing portion (11) including an amplifier (14) for amplifying the detector signal (13), a low-pass filter (16) for providing a running average (19) of the amplified detector signal (15), and a subtracting means (17) for generating a difference signal (18) from the amplified detector signal (15) and the running average (19),
a digital signal processing portion (12) for digitizing and
digitally processing the difference signal (18), and
a switch (23) controllable to short-circuit the input of the amplifier (14),
the digital signal processing portion (12) being adapted to calculate a transfer function of the analog signal processing portion (11) from the digitized difference signal (20) received in response to short-circuiting the input of the amplifier (14) at a given time when solely the reference carrier fluid passes the measuring cell (7), and the digital signal processing portion (12) being further adapted to recover the detector signal in a digital form by deconvoluting the digitized difference signal (20) with the transfer function.

2. A method for operating a thermal conductivity detector (5) comprising:

passing a sample fluid in a reference carrier fluid stream (1) through a measuring cell (7) and generating a detector signal (13) by means of a thermal conductivity detector element (8),
processing the detector signal (13) in an analog signal processing portion (11) including amplifying the detector signal (13), providing a running average (19) of the amplified detector signal (15) by low-pass filtering, and generating a difference signal (18) from the amplified detector signal (15) and the running average (19), and
digitizing and digitally processing the difference

signal (18),
the method further comprising, as an initial step, short-circuiting the input of the amplifier (14) at a given time when solely the reference carrier fluid passes the measuring cell (7) and calculating a transfer function of the analog signal processing portion (11) from the digitized difference signal (20) received in response to short-circuiting the input of the amplifier (14),
the step of digitally processing the difference signal including recovering the detector signal in a digital form by deconvoluting the digitized difference signal (18) with the transfer function.

3. A gas chromatograph comprising at least one thermal conductivity detector (5) of claim 1.

FIG. 1

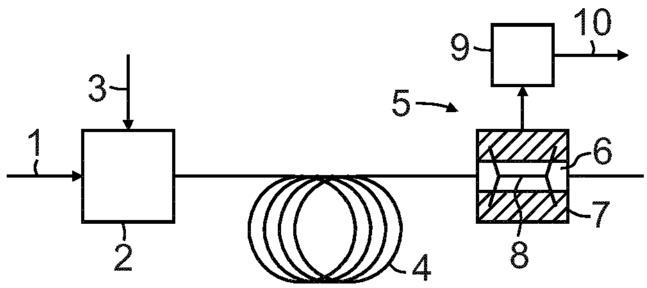
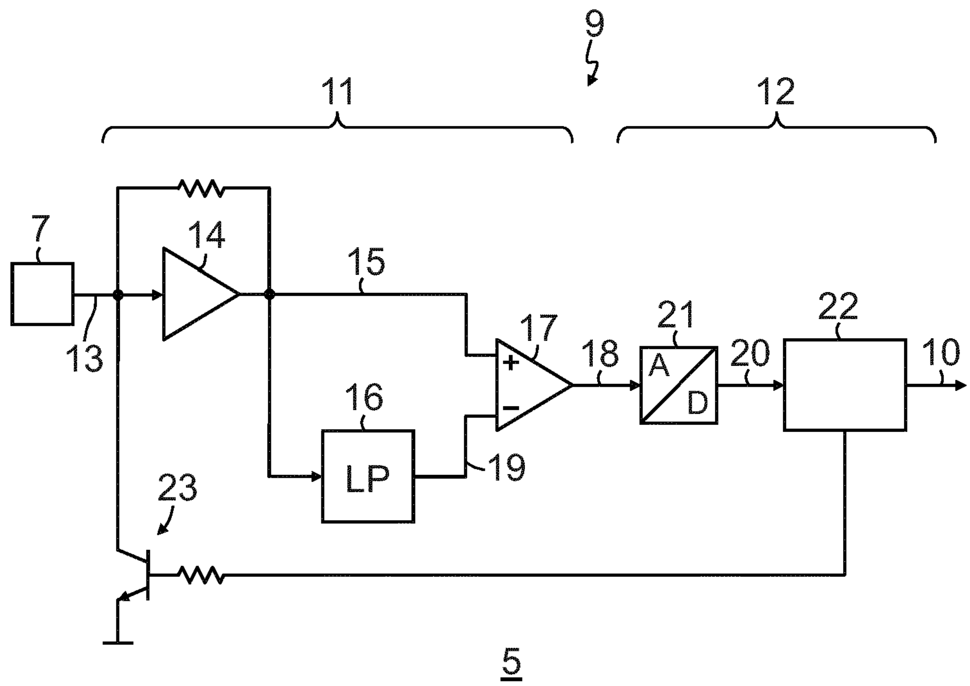


FIG. 2



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EUROPEAN SEARCH REPORT

Application Number
EP 14 16 4552

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
A	US 3 714 591 A (ALLINGTON R) 30 January 1973 (1973-01-30) * abstract * * column 3, line 13 - line 67 * * column 4, line 1 - line 65 * * column 6, line 9 - column 7, line 12 * * column 8, line 35 - line 40 * * figures 1-2 * -----	1-3	INV. G01N30/66 G01D3/032 G01D3/036 G01K7/02 G01K7/14 H03F1/30 ADD. G01N30/86
A	WO 2012/021681 A2 (SIEMENS INDUSTRY INC [US]; SCHMIDT GLEN EUGENE [US]; CORDILL LEROY DAV) 16 February 2012 (2012-02-16) * abstract * * paragraph [0042] * * figure 2 * -----	1-3	
A	DE 43 10 384 A1 (ABSTRON ELECTRONICS GMBH [DE]) 6 October 1994 (1994-10-06) * the whole document * -----	1,2	
A	GB 1 557 968 A (NORONIX LTD) 19 December 1979 (1979-12-19) * page 1, line 34 - line 64 * * page 2, line 96 - line 124 * * figures 1-2 * -----	1,2	TECHNICAL FIELDS SEARCHED (IPC) G01N G01D G01K H03F

The present search report has been drawn up for all claims

1

Place of search	Date of completion of the search	Examiner
Munich	17 June 2014	Bravin, Michel

CATEGORY OF CITED DOCUMENTS

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ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 14 16 4552

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17-06-2014

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WO 2012021681	A2	16-02-2012	NONE	
DE 4310384	A1	06-10-1994	NONE	
GB 1557968	A	19-12-1979	NONE	

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For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

REFERENCES CITED IN THE DESCRIPTION

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- US 20080291966 A1 **[0004]**